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SINGLE COLLISION GAS-SURFACE VIBRATIONAL ENERGY TRANSFER IN A R--ETC(U)

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Single Collision Gas-Surface Vibrational
Energy Transfer in a Reacting System

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Single Collision Gas-Surface Vibrational Energy Transfer
in a Reacting System^{*}

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Abstract

Gas-surface vibrational energy accommodation in a reactive system has been studied under single collision conditions. The reaction system is the isomerization of cyclobutene to 1,3-butadiene. Both seasoned pyrex and silica surfaces were used over the temperature ranges 400-775 K and 500-975 K, respectively. Strong collider behavior was observed below ~ 425 K. The vibrational energy accommodation coefficient was found to decrease with rise of temperature from ~ 1.0 to 0.2, while the relative collisional efficiency β_1 declined from ~ 1.0 to 0.008. A stochastic model was used to fit the data.

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Introduction

Gas-surface vibrational energy accommodation has been a subject of considerable interest both experimentally and theoretically.^{1,2} However, to this time there have been no single-collision measurements of gas-surface energy transfer in a high temperature reactive system.³ In the present communication, we describe the application of the Variable Encounter Method (VEM)⁴⁻⁸ to the study of single collision measurements with seasoned heated glass surfaces. Although such a surface is not well defined, it is the conventional experimental surface of thermal unimolecular kinetics.

The VEM technique has previously been applied to the study of energy transients: molecules are thermally equilibrated at some low temperature before experiencing an encounter, i.e. a sequence of m collisions (where m is variable and is chosen to be 1 in the present study) with a hot reactor surface; after the encounter, unreacted molecules are reequilibrated at the original low temperature. The amount of gas phase unimolecular reaction that occurs following surface activation gives the fraction of those molecules in the original Boltzmann distribution N_c that have been transported to energy levels above the critical reaction threshold, E_0 . As m increases, N_c approaches N_{ss} , the steady state population distribution characteristic of reactive depletion at the reactor temperature.

In the present work, the hot surface is convex in shape, ensuring that only a single collision occurs on encounter of the molecule with the surface. The single collision case has the advantage over previous multicollision VEM work (where $m = \sum_{n=1}^{\infty} nf(n)$), in that no averaging over some normalized distribution $f(n)$ of numbers of collisions made by the molecule per encounter with the reactor is necessary in the deconvolution of the data. This provides greater experimental stringency and constraints on suitable models for the collisional transition probability matrix, P . The present study also

permits a more direct evaluation of the gas-surface vibrational energy accommodation coefficient, α .

The ring-opening unimolecular isomerization of cyclobutene to 1,3 butadiene has a low⁹ E_0 (32.4 kcal mole⁻¹) and is substantially in the low pressure region at typical experimental pressures, $1 - 5 \times 10^{-4}$ torr. The reaction proceeds with no indication of surface catalysis.^{7,8} On the basis of the increasing strength of collision with decreasing temperature that was observed in earlier VEM studies, these characteristics make this species suitable for single collision study, and a significant amount of reaction should occur at lower temperatures.

Experimental

The reactant cyclobutene was 99.9% pure. The reactor is shown schematically in Fig. 1. The reaction vessel consisted of a 3 l pyrex flask with an internally heated, central reactor finger, A. Two different reaction vessels were used, fitted with pyrex and silica reaction fingers, respectively. The vessel wall was cooled by an ice bath. Liquid Bi-Pb-Sn eutectic was used as the internal bath medium (D) in the reactor finger and the top and bottom regions were heated independently (C) to minimize axial temperature variations. At the highest temperature (970 K) the maximum deviation was $\pm 5^\circ\text{C}$ and was significantly less at lower temperatures. Temperature measurements were made with calibrated chromel-alumel thermocouples (B). Before kinetic measurements were made, the reactor was "seasoned" at 750 K by pre-exposure for several hours to cyclobutene at a pressure of $\sim 5 \times 10^{-3}$ torr.

The system was run in both static and flow modes. In the former, the reactor was pumped to $< 10^{-6}$ torr and substrate was admitted at a pressure between 10^{-4} - 10^{-3} torr. The gas was pumped out and analyzed after a predetermined run time. For flow-mode runs, the impedance of a variable exit control valve was calibrated by pressure-drop measurements. A substrate entry flow control provided gas delivery rates of 2.5×10^{-2} to 0.22 torr cc s $^{-1}$. Typical residence times were 10 to 100 s, and pressure rose from $< 10^{-6}$ to $< 10^{-3}$ torr during a run, which was terminated by closing the variable flow stopcock after about 30 to 60 s. Pressure measurements were made with an MKS Model 170 capacitance manometer.

Product analysis was performed by gas-liquid chromatography on a 5' x 3/16" squalane column at 0°C with FID.

Results and Discussion

The probability of reaction per collision, P_c , was calculated from the product yield in both static and flow (Appendix) cases, and is plotted as a function of temperature in Fig. 2. Uncertainties in P_c varied from about $\pm 7\%$ at the highest to $\pm 20\%$ at the lowest temperatures. This is due to the greater temperature sensitivity at the lower temperatures. Also shown is a strong collider curve, calculated on the basis of the vibration frequency assignments of Elliott and Frey.⁹ The experimental curves coalesce at lower temperature where strong collider behavior is approached. At higher temperatures, slightly larger reaction probabilities were obtained with the pyrex reactor finger. Although the difference between the experimental curves is small, it exceeds the experimental uncertainty at the higher temperatures, and appears to represent either a minor difference in the rate of energy transfer on the pyrex-based vs silica-based surfaces or, possibly, a small difference in the preparation and seasoning procedures for the two fingers.

The mathematical models usually used to interpret energy transfer data both in conventional thermal¹⁰ and VEM⁴ systems give the probability, $P(\Delta E)$, of a down-transition of magnitude ΔE by the substrate molecule as an exponential (eq. 1) or gaussian (eq. 2) function:

$$P(\Delta E) = c_1 \exp (-\Delta E / \langle \Delta E \rangle) \quad (1)$$

or

$$P(\Delta E) = c_2 \exp (-(\Delta E - \Delta E_{mp})^2 / 2\sigma^2) \quad (2)$$

where $\langle \Delta E \rangle$, ΔE_{mp} and σ are adjustable parameters and the c 's are constants. These functions, along with the detailed balance and completeness relations, specify P_c .¹¹ However, these forms are inadequate to describe near-strong collider behavior. As strong collider behavior is approached, the columns of P should approach normalized Boltzmann vectors B characteristic of the reactor

temperature, T_r , i.e. $p_{i+j} = B_i$, for all i, j ; this condition is clearly not met by eq. 1 or 2. All choices of parameters with these models give values of P_c that are significantly below strong collider and the present observed values. The Boltzmann-weighted exponential (BE)(eq. 3) does fit the data and gives the correct strong collider limiting behavior; here

$$p_{i+j} = c_3 \exp(-\Delta E / \langle \Delta E \rangle) g_i \exp(-E_i / kT_r) \quad (3)$$

g_i is the density of vibrational states at level E_i ,
and c_3 is a constant.

The calculated average amount of energy $\langle \Delta E' \rangle_{E_0}$ transferred in a down step from hot molecules at the level of energy E_0 is shown in Table II for several reactor temperatures. Still another quantity of interest is the average energy transfer, ΔE_{av} , defined as the difference in average energies of substrate molecules before, \bar{E}_i , and after, \bar{E}_f , collision; \bar{E}_i refers to the flask temperature (273K). This is related to the vibrational accommodation coefficient $\alpha = \Delta E_{av} / (\bar{E}_r - \bar{E}_i)$, where \bar{E}_r is the average energy of substrate molecules at the reactor finger temperature. Values of α and of ΔE_{av} are given in Table I. Also given are values of the collisional efficiency β_1 , defined as $\beta_1 = P_c / P(sc)$, as well as efficiencies β_{ss} that would be observed in an equivalent steady state thermal system; $\beta_{ss} = P(\infty) / P(sc)$, where $P(\infty)$ is the actual steady-state reaction probability per collision and $P(sc)$ is the strong-collider value of the reaction probability per collision. β_{ss} is the same value that would apply in a low-pressure gas-phase thermal unimolecular system where it is defined as $\beta_{ss} = k_o^{wc} / k_o^{sc}$; $\omega^{wc} = \omega^{sc}$; or equivalently as $\beta_{ss} = \omega^{sc} / \omega^{wc}$, $k_o^{wc} = k_o^{sc}$; here k_o^{wc} , k_o^{sc} are the observed low pressure rate constants measured at constant collision frequencies ω^{wc} and ω^{sc} in a weak collider and strong collider system, respectively. It is evident from Table I that since

the β_{ss} values group close to unity at all temperatures, a less stringent test of energy transfer behavior is available in steady-state experiments as compared to the present measurements of β_1 in the transient region. In reactive systems, β_1 is also a more sensitive function of energy transfer efficiency than is α , since the former tests efficiency relative to the difference, $E_0 - \bar{E}_i$, while the latter tests efficiency relative to the difference, $\bar{E}_r - \bar{E}_i$.

The decline in collisional efficiency that occurs with rise of temperature in Fig. 2 and Table I has been observed previously in cyclobutene VEM studies^{7,8} where strong collider behavior was inferred below ~ 450 K, as has been found here. This same general trend has been observed in all VEM studies and in conventional homogeneous thermal studies at higher temperatures. It is also generally observed in energy accommodation studies.¹ This trend appears to be related to the fact that as the temperature is lowered the time that the molecule spends trapped in the gas-surface potential well increases. The Boltzmann-weighted models then correspond more closely to the case of statistical accommodation on the surface, with relaxation of the restrictions on conservation of angular momentum that apply in gas-gas systems.¹²

Draper and Rosenblatt measured vibrational energy accommodation coefficients of hydrocarbons on metal surfaces at room temperature by a vibrating diaphragm technique.² Although those experiments are not directly comparable to ours, we note that their values of α_{vib} are fairly close to unity, i.e., 0.7 to 0.8. For larger molecules, i.e., as the depth of the potential well increased, they found that the values of α_{vib} also increased.

One final comment: the present data on energy transfer efficiency extend upward from 425 K; the low temperature region from ~ 200 to ~ 700 K is one that has previously been explored in thermal, chemical activation and photo-excitation reactive systems with conflicting conclusions as to whether efficiency increases or decreases with rise of temperature.¹⁰ The present system reveals marked decrease in $\langle \Delta E' \rangle$, β_1 and α in this region with rise of temperature.

Table I. Energy transfer parameters in the cyclobutene system^a

	T(K)					
	<u>400</u> ^b	<u>500</u>	<u>600</u>	<u>750</u>	<u>875</u>	<u>975</u>
$\langle \Delta E \rangle_{E_0} (\text{cm}^{-1})$	10,550	8940	6925 (7520)	4200 (4700)	3125	2540
$\Delta E_{av} (\text{cm}^{-1})$	465	720	780 (900)	900 (1000)	1050	1135
α	1.0	0.57	0.40 (0.47)	0.28 (0.31)	0.23	0.20
β_{ss}	1.0	1.0	0.994 (0.998)	0.87 (0.92)	0.68	0.51
β_1	1.0	0.40	0.14 (0.22)	0.029 (0.048)	0.0134	0.008

a) Parenthetic values apply to the pyrex reactor. Pyrex and silica reactors give indistinguishable results at 500 K.

b) Strong collider behavior

Appendix. Flow system: apparent rate constant.

Mass conservation requires

$$V \frac{dR}{dt} = Q' - F'R - kVR \quad \text{and} \quad V \frac{dP}{dt} = -F'P + kVR,$$

where $R(t)$ and $P(t)$ are the concentrations of reactants and products at time t , respectively; Q' is the flux of reactant into the reaction vessel of volume V ; k is the apparent rate constant ($= P_c \bar{c} A/4V$, where \bar{c} is the mean molecular speed and A is the heated reactor area); and F' is the Knudsen output flow impedance. Since the reactor is initially evacuated, $P(0) = 0$, $R(0) = 0$. The amount of product collected, P_T , is given by

$$P_T = F' \int_0^{t_m} P(t) dt$$

where t_m is the run time. An analogous expression applies for the amount of reactant collected R_T . One obtains

$$\frac{R_T}{R_T + P_T} = \frac{F}{F+k} \frac{t_m - \frac{1}{F+k} [1 - \exp(-(F+k)t_m)]}{t_m - \frac{1}{F} [1 - \exp(-F t_m)]}$$

where $F = F'/V$. This equation may be solved iteratively for k .

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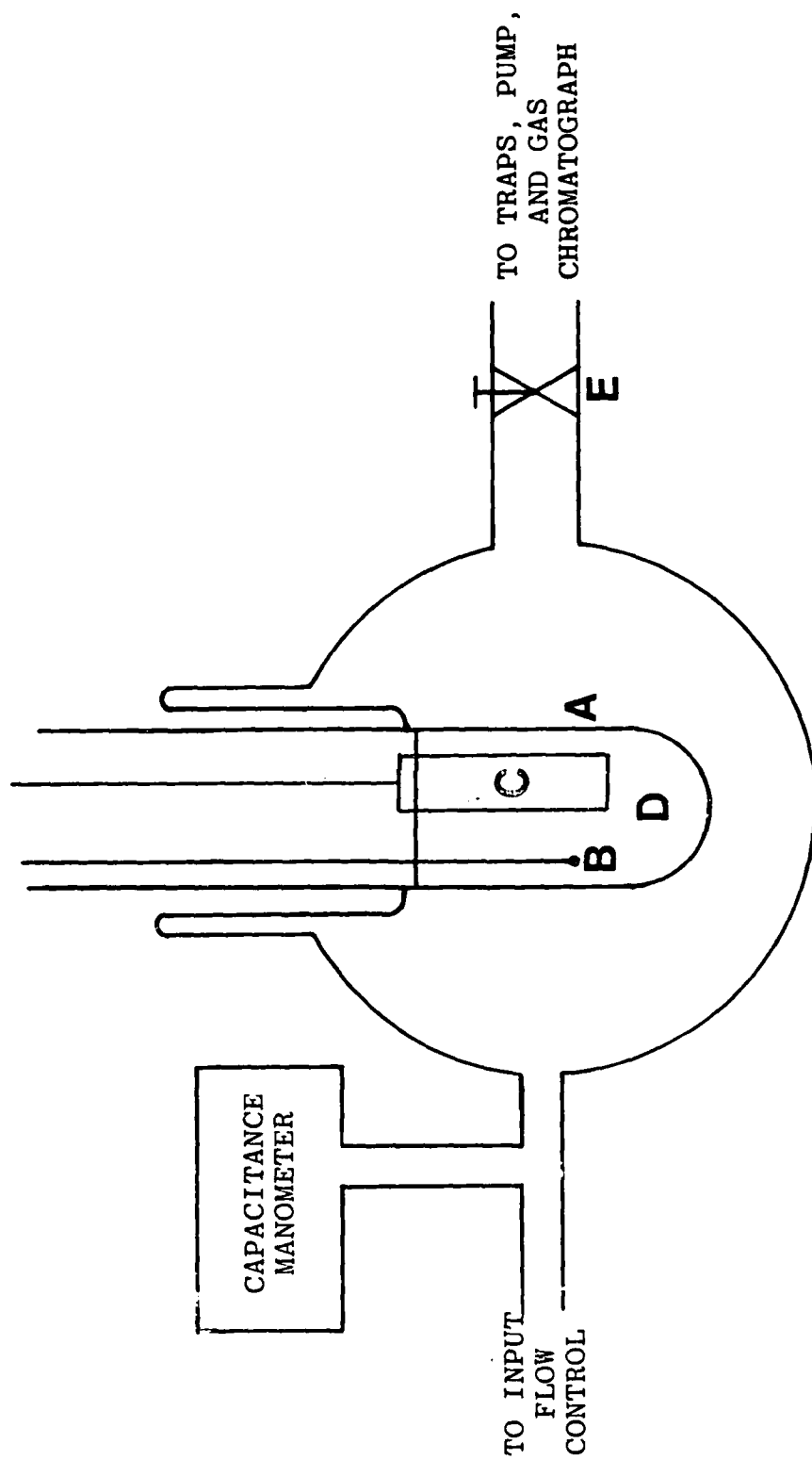
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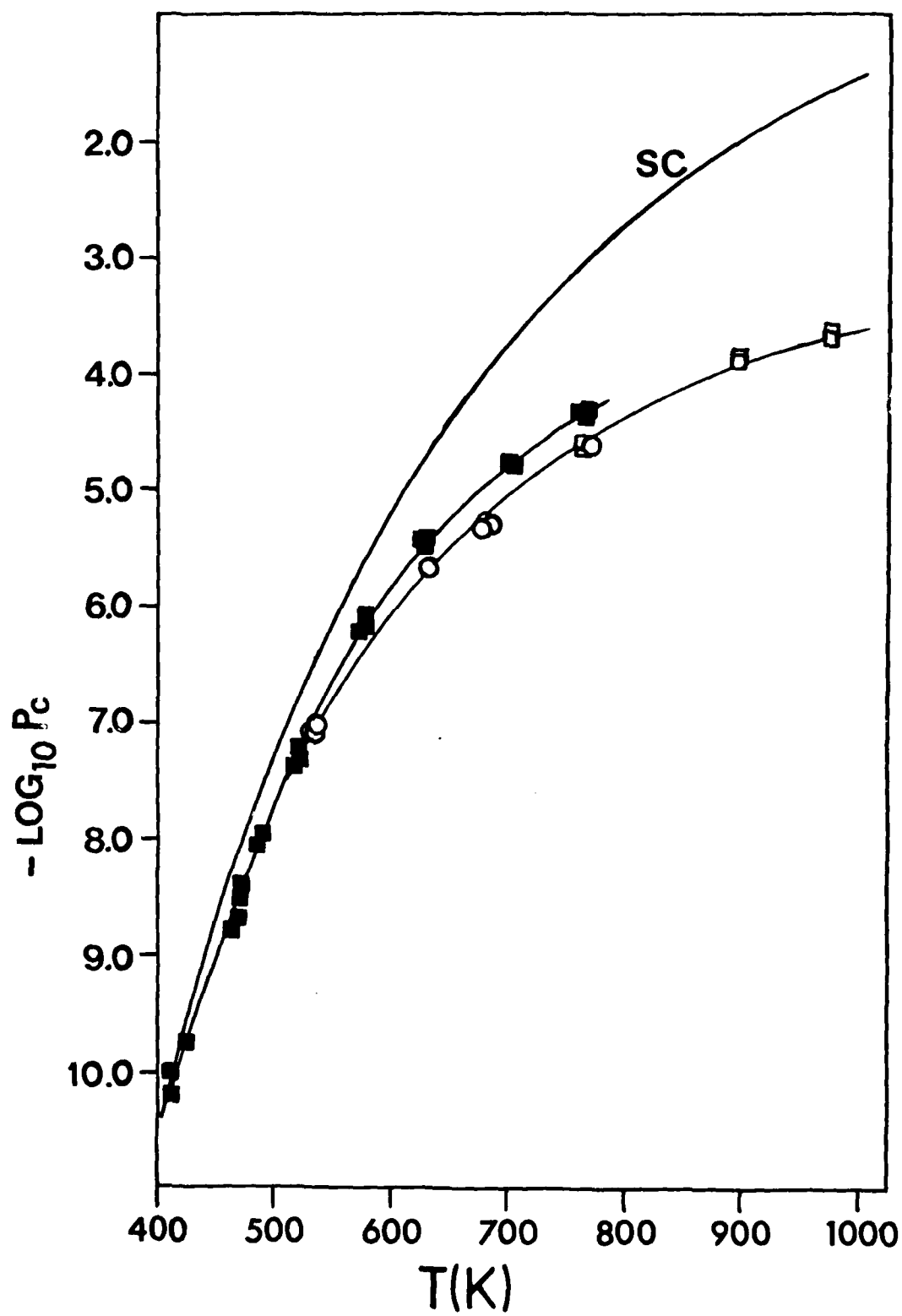
Figure Captions

Figure 1. Schematic of single collision VEM reactor. Shown are pyrex (or silica) reactor finger, A; moveable chromel-alumel thermocouple, B; heaters, C, in two sections, top and bottom; eutectic bath, O; and variable flow stopcock, E.

Figure 2. Plots of experimental values of P_c vs T for the following reactors and conditions: pyrex, static, \blacksquare ; silica, static, \bigcirc ; and silica, flow, \square . Also shown is a calculated strong collider (SC) curve. The magnitudes of random errors are approximately given by the size of the symbols. The magnitude of unspecified systematic errors may be judged from the scatter of the data; such errors are largest at low temperatures and are believed to be primarily due to error in temperature (see text).



3 L PYREX VESSEL



were used over the temperature ranges 400-775 K and 500-942 K, respectively. Strong collider behavior was observed below 425 K. The vibrational energy accommodation coefficient was found to decrease with rise of temperature from 1.0 to 0.2, while the relative collisional efficiency declined from 1.0 to 0.008. A stochastic model was used to fit the data. *beta sub 1*

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